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SIMPLIFIED VOLATILE ORGANICS SAMPLER

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Organic Compounds	Toxicity	Stationary Sources	07C 06T
Volatility	Sorbents	Volatile Organic Compounds (VOCs)	20M 11G
Sampling	Gas Chromatography	Hazardous Waste	14B 07D
Analyzing	Mass Spectroscopy		14G 07B
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FOREWORD

This report has been prepared by Southern Research Institute as part of ongoing studies in support of regulatory programs of the Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory at Research Triangle Park, North Carolina. This report contains data describing the evaluation of a Tenax-GC/Spherocarb tandem-bed sorbent tube for sampling of volatile organic compounds. The data in this report are intended to demonstrate the feasibility of a simplified design for a sampling system for medium levels of volatile organic compounds. The sample-collection system is intended for use by laboratories engaged in engineering projects that require semiroutine monitoring of hazardous-waste streams of incineration facilities.

ABSTRACT

As part of the Resource Conservation and Recovery Act (RCRA) of 1976, the U.S. Environmental Protection Agency (EPA) has proposed regulations for owners and operators of facilities that treat hazardous wastes by incineration to ensure that these incinerators will be operated in an environmentally responsible manner. The primary criterion upon which the operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. The DRE value, defined in terms of waste-input and stack-output levels of designated principal organic hazardous constituents (POHCs), must be equal to or greater than 99.99%.

The volatile organic sampling train (VOST) was originally designed to sample very low levels of volatile materials in incinerator effluents. A simplified system is needed to support engineering projects for hazardous-waste combustion requiring numerous semiroutine sampling tests. The purpose of this study was to provide a design for a simplified sampling system for medium levels of volatile organic compounds.

A major part of this study has been the evaluation of sorbents and mixed-sorbent sampling tubes for a rugged, compact volatile organic-collection system. This report contains the evaluation of sorbent materials, the development of a sampling tube, and the laboratory evaluation of the sampling system with several volatile organic compounds. The simplified sampling system consists of a single tandem-bed sorbent tube containing Tenax GC and Spherocarb sorbents. Direct thermal desorption into a GC/FID or GC/MS provides a rugged and simple sampling and analysis system.

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ABBREVIATIONS AND SYMBOLS

amu	Atomic Mass Unit
Bz	Benzene
CCl ₄	Carbon Tetrachloride
CFR	Code of Federal Regulations
ClBz	Chlorobenzene
cm	Centimeter
DRE	Destruction and Removal Efficiency
EI	Electron Impact Ionization Mode
EPA	U.S. Environmental Protection Agency
g	Gram
GC	Gas Chromatography
GC/FID	Gas Chromatography/Flame-Ionization Detection
GC/MS	Gas Chromatography/Mass Spectrometry
h	Hour
ID	Internal Diameter
is	Internal Standard
L	Liter
L/min	Liter per Minute
LOD	Limit of Detection
µg	Microgram (10 ⁻⁶ g)
µg/g	Microgram per Gram
µL	Microliter (10 ⁻⁶ L)
µg/m ³	Microgram per Cubic Meter
min	Minute
mg	Milligram (10 ⁻³ g)
mL	Milliliter (10 ⁻³ L)
m ² /g	Square Meter per Gram
mm	Millimeter (10 ⁻³ m)
mol wt	Molecular Weight
MRI	Midwest Research Institute
m/z	Mass to Charge Ratio
ng	Nanogram (10 ⁻⁹ g)
ng/L	Nanogram per Liter
nm	Nanometer (10 ⁻⁹ m)
OD	Outside Diameter
PAT	Purge and Trap
POHC	Principal Organic Hazardous Constituent(s)
PIC	Product(s) of Incomplete Combustion
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RRF	Relative Response Factor
RSD	Relative Standard Deviation
s	Second
SD	Standard Deviation
SoRI	Southern Research Institute
TCE	Trichloroethylene
THF	Tetrahydrofuran
Tol	Toluene
t _r	Retention time
v	Volume
VOST	Volatile Organic Sampling Train

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SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) (1) requires owners/operators of facilities that incinerate hazardous waste to ensure that their incinerators are operated in an environmentally safe manner. The Code of Federal Regulations, Title 40, part 264, requires that a destruction and removal efficiency (DRE) of 99.99% be achieved for each principal organic hazardous constituent (POHC) monitored during a trial burn.

The DRE standard requires sampling and analysis to quantify POHCs in the waste-feed material and stack-gas effluent. The methods manual ("Sampling and Analysis Methods for Hazardous Waste Combustion") provides information on methods that are applicable to process streams of hazardous-waste combustion units (2).

The results of previous trial burns of hazardous-waste incinerators suggest that volatile POHCs and volatile products of incomplete combustion (PICs) may be important components in incinerator effluents. The collection and determination of volatile organic compounds boiling at less than 100 °C has been achieved by using bags, bulbs, and the volatile organic sampling train (VOST). The methods manual provides information on these methods. A protocol for the VOST has been developed (3) which allows the sampling and analysis of POHCs with sufficient sensitivity to calculate a DRE of equal to or greater than 99.99% when the POHCs are present in the waste feed at 100 µg/g or higher. The VOST protocol uses multiple sorbent traps with Tenax-GC/charcoal for sampling the stack effluents. Analysis with desorption through a purge-and-trap (PAT) apparatus reduces water input into the chromatographic column. Detection and quantification of the POHCs are performed by mass spectrometry. The VOST thus provides increased sensitivity to low-level concentrations of volatile POHCs because of its ability to concentrate the gaseous effluent.

The purpose of this study is to provide the foundation for a simplified sampling-and-analysis system for medium concentration levels of volatile organic compounds. We examined sorbent systems that would reduce the number of sorbent tubes and the complexity of the sampling system. We also examined desorption methods that would eliminate the need for PAT desorption of sorbent tubes. Our objective was to provide sensitivity sufficient to permit calculation of a DRE equal to or greater than 99.99% when POHCs are present in the waste feed at 1000 µg/g or higher.

This report describes the preliminary development of a tandem-bed sorbent system using a single sorbent tube and thermal desorption. PAT desorption is not required in this proposed system. Laboratory evaluations of the sampling-and-analysis system were performed with candidate volatile POHCs.

SECTION 2

CONCLUSIONS

The simplified volatile organic sampling system developed in this study should be a useful addition to the existing protocols for sampling and analysis of volatile organic compounds in incinerator effluents. This sampler is not a replacement for VOST but is intended to provide a simple method of sampling for use when extremely low levels of detection for POHCs are not required. It allows the sampling and analysis of compounds boiling under 150 °C with adequate recoveries (45 to 102%) and detection capabilities (LOD 5 to 50 ng). The simplified sampling system consists of a single tandem-bed sorbent tube containing Tenax-GC and Spherocarb sorbents. Direct thermal desorption into a GC/FID or GC/MS provides a rugged and simple sampling and analysis system.

SECTION 3

RECOMMENDATIONS

Based on the laboratory evaluation of the simplified sampling-and-analysis system and on the resulting percent recoveries of selected candidate POHCs, recommendations for future investigations are as follows.

- Extend the laboratory evaluation of the sampling system to other volatile POHCs and PICs and incorporate internal standards into the analytical procedure.
- Construct a prototype of a field sampler based on the laboratory system.
- Develop a draft protocol for evaluation of the prototype field sampler in the laboratory.
- Conduct field studies of the prototype system at experimental research incineration facilities.
- Finally, utilize multicomponent gaseous standards for calibration and quality control of the sampling-and-analysis system.

SECTION 4

TECHNICAL APPROACH

BACKGROUND

The regulations for hazardous-waste incineration include the requirement that, for selected POHCs, a destruction/removal efficiency (DRE) equal to or greater than 99.99% must be achieved. To meet the need for reliable sampling and analysis method, the VOST was developed by EPA as an alternative to the use of integrated gas bulbs and bags. Midwest Research Institute (MRI) carried out the laboratory study to develop and evaluate the sampling-train concept (4). Subsequently MRI evaluated a field version of the sampler under field conditions. The VOST which was evaluated consisted of a system to draw effluent gas at a flow rate of 1 L/min through two traps (1.6-cm ID x 10 cm) in series. The first trap contained Tenax-GC and was preceded by a gas cooler and followed by an impinger. A second trap containing Tenax-GC and charcoal was located after the impinger. Figure 1 is a schematic of the VOST. This arrangement requires replacing both pairs of traps with fresh traps every 20 min (20-L sample) over a 2-h sampling period for a total of six pairs of traps. The changing of the traps prevents breakthrough of volatile compounds and also allows the initial analysis of one pair of traps, thus lowering the possibility of overloading the GC/MS system. The remaining tubes can be combined to increase sensitivity when low concentrations of POHCs are present.

The sensitivity of the VOST method is dependent upon the level of interferences in the sample and the presence of detectable levels of volatile POHCs in blanks. The target detection limit of this method is $0.1 \mu\text{g}/\text{m}^3$ ($0.1 \text{ ng}/\text{L}$) of flue gas. This detection limit permits calculation of a DRE equal to or greater than 99.99% for those volatile POHCs which may be present in the waste feed streams at $100 \mu\text{g}/\text{g}$. Laboratory development data (4) have demonstrated a range of 0.1 to $100 \mu\text{g}/\text{m}^3$ (0.1 to $100 \text{ ng}/\text{L}$) for selected volatile POHCs.

As with all systems for trace-gas analyses, major problems can develop. These include leaks in the systems, background contamination, cleanup of sorbents and breakage of sorbent tubes. Protection of the integrity of the sample components is essential. Blanks and standards run at frequent intervals are necessary safeguards against contamination on the one hand and loss on the other.

EPA has monitored the performance of the VOST and developed a protocol for the collection and analysis of volatile POHCs using VOST (3). Also, Environmental Monitoring System Laboratory, Research Triangle Park has sponsored laboratory validation studies and field test validation studies of the VOST (5, 6). The position of the VOST in support of the hazardous-waste-incineration program is established. However, many incinerators and combustion facilities are operating with higher concentrations of feed to the incinerator. Likewise, many engineering studies do not require the use or detection of extremely low concentrations of volatile organics. Therefore, a simplified sampling system that does not replace VOST but meets the needs of operators with less demanding criteria is needed.

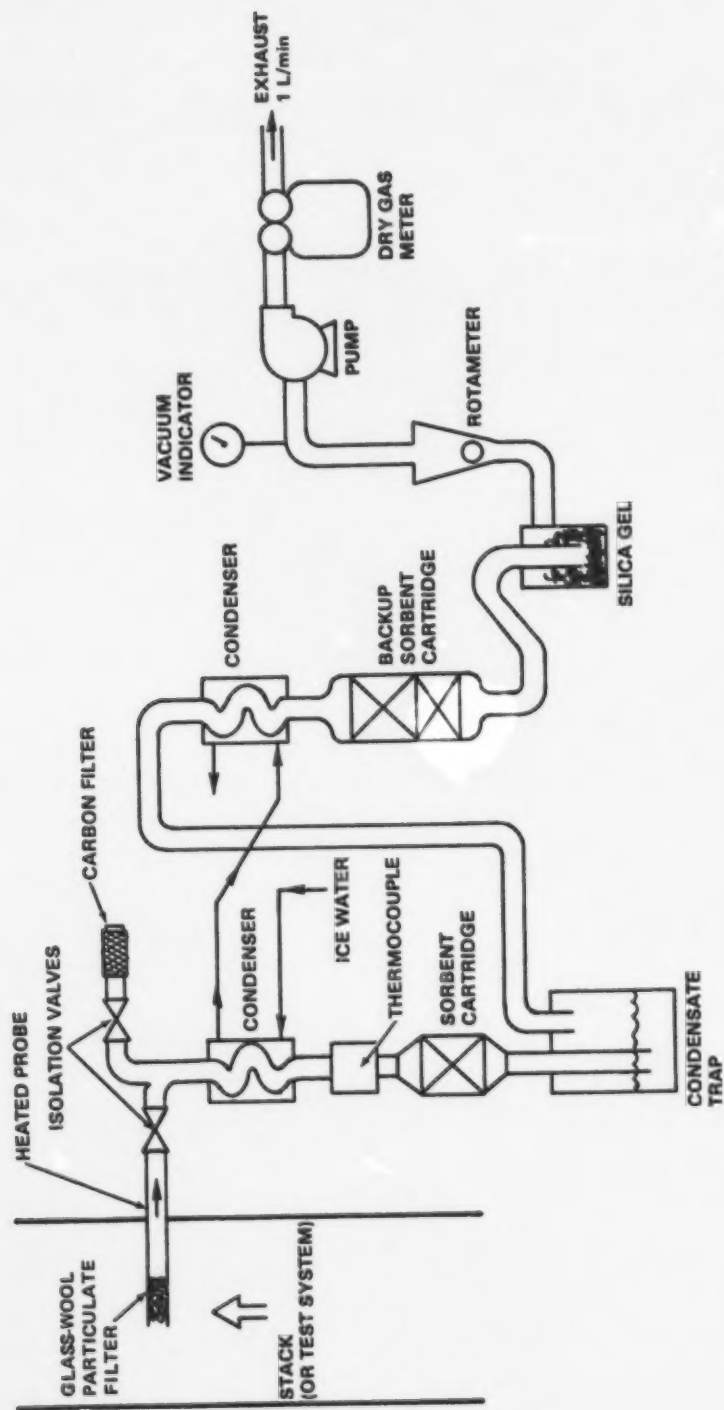


Figure 1. Schematic of volatile organic sampling train (VOST).

Likely candidates for review included the selection of a solid sorbent, the design of the sorbent tube, and the method of desorption to the GC/MS system. Our experimental goals were to develop a methodology to permit the determination of a DRE of greater than or equal to 99.99% for hazardous-waste streams containing selected POHCs at a concentration $>1000 \mu\text{g/g}$.

Approach

The VOST that was initially evaluated by MRI (4) consisted of two traps. The first one contained Tenax and was preceded by a gas cooler/condenser. Following the trap was an impinger for condensate collection. The second trap contained a section of Tenax followed by a section of charcoal as a backup sorbent. Compounds of relatively high volatility were collected in the second trap. Also, to ensure that more volatile compounds did not break through both traps, the traps were replaced every 20 min throughout a 2-h sampling period.

Several possibilities are available to provide an alternate sampling system. Newer sorbent media with different physical properties may be placed in the traps. The amount of sorbent material used may also be varied.

Objective

A sampler for volatile organic compounds that will be used in engineering projects must be portable and rugged so that it can be transported from the laboratory to the field site and returned to the laboratory. Also, the sampler must be simple to operate. The geometric design of the sampler should be compatible with the systems in the field that are being monitored. The sampler must be able to collect and retain the organic compounds of interest. At the time of analysis, the organic compounds must be easily desorbed from the sorbent traps.

Criteria for Selection of Solid Sorbents

Trace enrichment of organics using sorption techniques can be described as the process by which the compounds of interest are concentrated by their selective removal from the sample matrix. Sorbents commonly used are Tenax-GC, XAD-2, carbon molecular sieves (CMS), silica gel, polyurethane foams, and charcoal. The chemical surface properties of the sorbent as well as particle size, pore volume, and surface area govern the ability of the sorbent to collect and

retain materials of interest. The chemical surface properties influence the basic selectivity of the sorbent. The particle size will affect the pressure drop across the sorbent bed and will also determine whether mass transfer from the gas phase to the particle will be rate limiting and thus affect the collection efficiency. Within a given adsorbent, the pore volume and surface area are interrelated. A larger surface area will usually lead to greater equilibrium adsorption capacity, but the surface must be available within the time allowed in the bed transport. Thus, adsorbents with low surface areas are sometimes more effective because they may have a larger amount of surface available in large pores where gas-phase diffusion will not be rate limiting. These characteristics influence the sample capacity and breakthrough volume of a sorbent and control its usefulness for a particular problem.

Activated charcoal is a commonly used solid sorbent. For a given amount of charcoal, the surface area and the adsorptive capacity are very high. Activated charcoal has a reactive surface and thus may not be suitable for reactive compounds. Silica gel is less reactive than charcoal, but because of its polar and hygroscopic characteristics, breakthrough capacity will decrease with increasing humidity. Porous polymers have a lower surface area and much less reactive surface than charcoal. Thus, adsorptive capacity is lower and reactivity is much lower for porous polymers. Ambersorb sorbents have characteristics that place them between those of charcoal and porous polymers. Molecular sieves are sorbents that retain adsorbed species according to their molecular size. Humidity is an important factor when using molecular sieves because water may displace the analyte from the sorbent.

EXPERIMENTAL

The primary focus of our experimental work was to evaluate five sorbents and two types of sampling tubes. GC/FID and GC/MS were used to determine the volatile organic compounds that were desorbed from the sampling tubes.

Selection of Solid Sorbents

After a review of the literature, we selected five sorbents that have been used successfully in sampling and were prime candidates for use in semiroutine sampling to support engineering projects.

We wanted to evaluate sorbents that may be more effective than Tenax-GC for collecting volatile organic compounds in the VOST. Thus, we screened five sorbents (Tenax-GC, Spherocarb, Ambersorb XE-340, Ambersorb XE-347, and Carbo-sieve G) using 3.8 cm of the sorbent material in 3- and 8-mm-OD sampling tubes. A description of these sorbents is summarized in Table 1. In the final sorbent-tube design, we used tandem-bed sorbents in the sampling tubes.

TABLE 1. DESCRIPTION OF SORBENT MATERIALS

Sorbent	Mesh	Surface area, m ² /g	Supplier	Description
Tenax-GC	60/80	19	Supelco	Polymer of 2,6-diphenyl- p-phenylene oxide
Spherocharb	60/80	1200	Analabs	Carbon molecular sieve spheres
Ambersorb XE-340	20/40	400	Rohm and Haas	Synthetic carbonaceous spheres
Ambersorb XE-347	20/40	350	Rohm and Haas	Synthetic carbonaceous spheres
Carbosieve G	60/80	-- ^a	Supelco	Carbon molecular sieve

^aNot available.

Preparation of Sorbent Tubes

We used two types of sorbent tubes for the sorbent screening. Initially, we used a 3-mm-OD x 11-cm glass tube filled with 3.8 cm of the sorbent. A minimum amount of glass wool was used in each end of the glass tube to hold the sorbent in place. Because of a limited capacity, the 3-mm-OD glass tube was later replaced with an 8-mm-OD glass tube. Figure 2 shows a drawing of the sorbent-tube sampler.

Construction of Test-Atmosphere Generator

We constructed a vapor-generator system capable of producing atmospheres containing volatile organic compounds: benzene, carbon tetrachloride, chlorobenzene, tetrahydrofuran, trichloroethylene, and vinyl chloride. The system utilized permeation tubes (Kin-Tek Laboratories, Inc., Texas City, TX) which provide a constant output of each of the compounds listed above. These permeation tubes consisted of short lengths (10 cm) of Teflon tubing with a liquid phase of the compound sealed inside. The permeation rate of the tube is a function of the temperature, the length of the tube membranes, the type of Teflon tubing used, and the wall thickness of the tubing. Certified permeation rates for each tube are listed in Table 2. Vapor from the tube was carried first into a mixing chamber and then to a sampling chamber with charcoal-filtered air. The concentration of the volatile organic compounds in the test atmosphere was controlled by adjusting the flow of dilution air that mixes with the vapor stream in the mixing chamber. The system also allows for the introduction of humidified air through a separate air stream. Figure 3 shows the vapor-generator system.

Design of the Sampling-and-Analysis System

As a result of our preliminary evaluations, we proposed the generalized sampling-and-analysis system given in Figures 4 and 5. The sampling system is made up of a probe, cooler/condenser, sorbent tube, condensate trap impinger, second sorbent tube (optional), rotometer, and pump. Because the system is intended for short sampling periods and condensate is not expected to be present, the condensate-trap impinger may be considered optional. If condensate does form and contain water-soluble volatiles, the condensate will have to be analyzed. The analytical system consists of a thermal-desorption unit, gas chromatograph, FID or MS detector, and data system.

Evaluation of Solid Sorbents

We screened five sorbent materials by spiking our prepared sorbent tubes with 4 μ L of a working standard solution. This resulted in the following amounts of each compound on the tubes: tetrahydrofuran--355 ng; carbon tetrachloride--639 ng; trichloroethylene--585 ng; benzene--350 ng; toluene--347 ng; and chlorobenzene--442 ng. Charcoal-filtered air was pulled through the tube at a rate of 0.28 L/min for 3-mm tubes and 0.5 L/min for 8-mm tubes to simulate sampling of standard atmospheres. Each tube was thermally desorbed

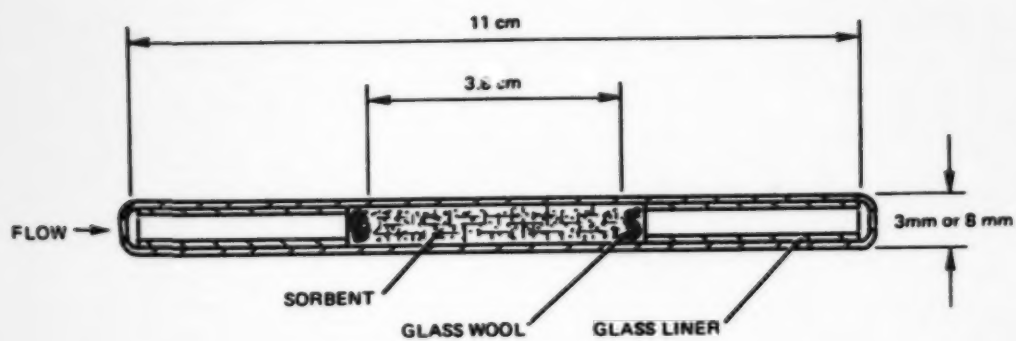


Figure 2. Drawing of sorbent-tube sampler.

TABLE 2. CERTIFIED PERMEATION RATES OF
GENERATOR PERMEATION TUBES^a

Compound	Temperature, °C	Permeation rate, ng/min
Benzene	60	4035
Carbon tetrachloride	60	3199
Chlorobenzene	60	2812
Tetrahydrofuran	60	2688
Trichloroethylene	40	539
Vinyl chloride	30	2654

^aCertified by Kin-Tek Laboratories, Inc., Texas City, TX.

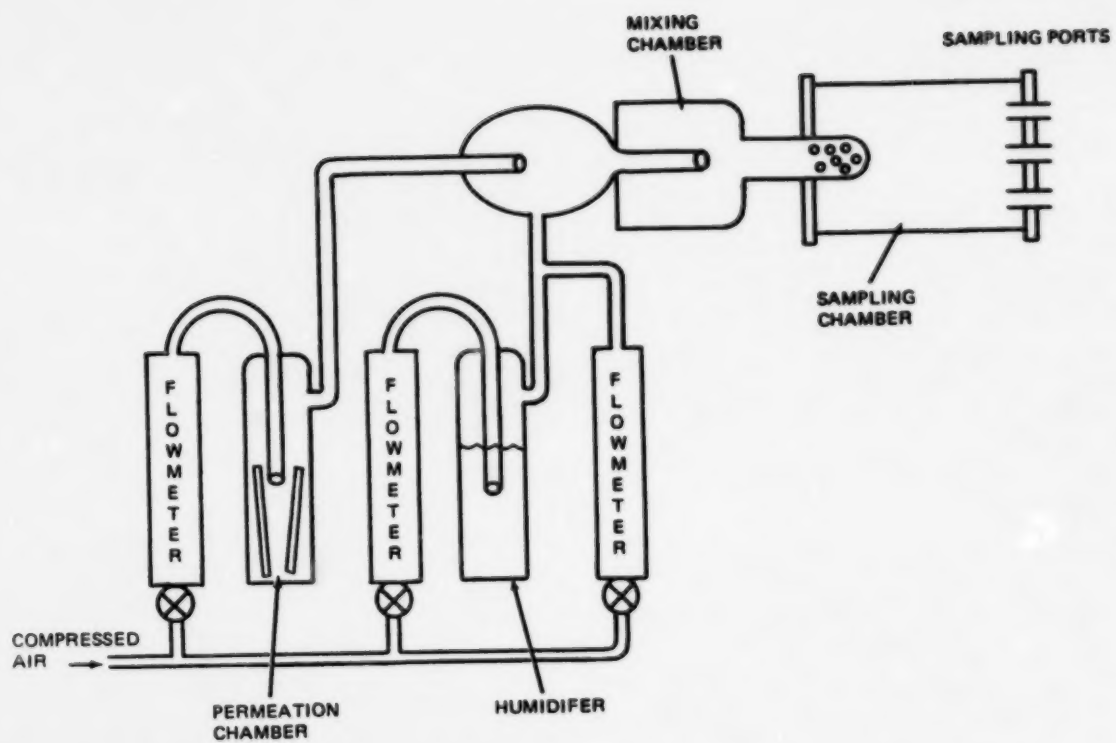


Figure 3. Vapor-generator system.

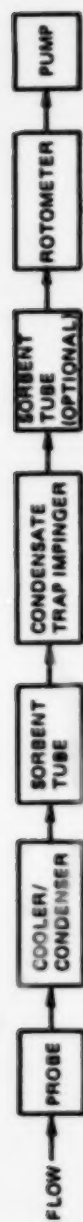


Figure 4. Block diagram of simplified volatile organics sampler.

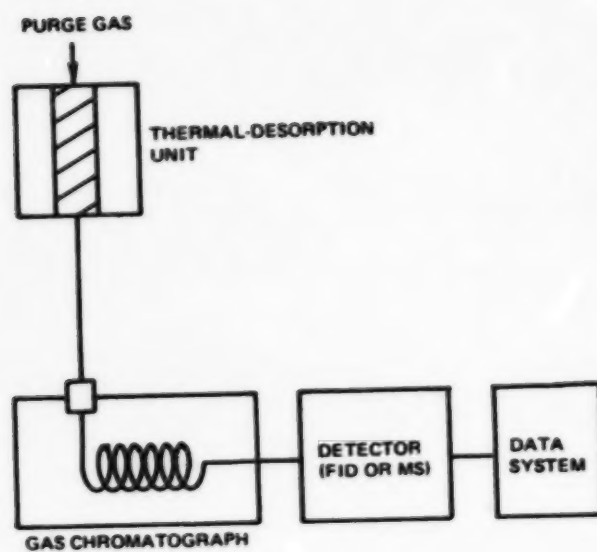


Figure 5. Block diagram of analytical system.

and analyzed by GC/FID to determine the recovery of volatile organic compounds from the sorbent when compared with the direct injections of the standard solution.

Prepared sorbent tubes were used to collect volatile organic compounds from an audit cylinder provided by EPA. The cylinder contained low concentrations of vinyl chloride, chloroform, carbon tetrachloride, benzene, and perchloroethylene in nitrogen. We sampled 2.5, 5.0, and 10 L from the audit cylinder at a sampling rate of 0.5 L/min. The sorbent tubes were then thermally desorbed and analyzed using the GC/FID and GC/MS. Concentrations were determined by comparing area responses of the audit cylinder samples to the area responses obtained from calibration standards of organic volatile compounds. We prepared calibration curves by spiking 2, 4, 6, and 8 μL of a standard solution (containing 294 $\mu\text{g/mL}$ chloroform, 317 $\mu\text{g/mL}$ carbon tetrachloride, 175 $\mu\text{g/mL}$ benzene, and 325 $\mu\text{g/mL}$ perchloroethylene in carbon disulfide) on sorbent tubes. The sorbent tubes were thermally desorbed into the GC/MS for analysis.

A vapor-generator system was used to prepare test atmospheres for measuring the capacity of the candidate sorbents. Between 5 and 30 L of a benzene/chlorobenzene (16 ppb each) atmosphere were sampled at a sampling rate of 0.5 L/min. Also, the vapor-generator system was used to produce the mixed-vapor concentrations of the six compounds listed in Table 3. We sampled 2.5, 7.5, and 15 L from the generated atmosphere with each type of sorbent tube at a sampling rate of 0.5 L/min.

To study the effect of humidity on the method, we spiked standard solutions containing six of the volatile organics on 8-mm, 1.9-cm-Tenax/1.9-cm-Spherocharb sorbent tubes. Charcoal-filtered air was pulled through the tubes either with or without subsequent humidification to simulate sampling. In further studies, a sodium sulfate pretube was used to remove moisture. In those studies, the standard was spiked onto the glass wool in front of the sodium sulfate. The filtered and humidified air was pulled through the pretube and the sample tube. Only the sample tube was desorbed for analysis.

Next, we investigated the effect of humidity on the determination of generated-vapor samples. We used the generator to simulate low concentrations of benzene and chlorobenzene atmospheres (16 ppb each) so that we could study the effects of humidity on the sampling method using 1.9-cm-Tenax/1.9-cm-Spherocharb tubes with Na_2SO_4 pretubes. The generator was operated at two levels of relative humidity: 50% and 75%. Samples were collected at a rate of 0.5 L/min, and the sample volumes ranged from ≈ 5 to 30 L.

We also tested the selected sorbent tube for stability. Duplicate tubes were used to sample 7.5 L from the generator at a sampling rate of 0.5 L/min. Then the tubes were analyzed by thermal-desorption GC/FID to establish the vapor concentration in the generator. The experiment was repeated except that the tubes were capped and stored for three days at room temperature and then analyzed by GC/FID.

TABLE 3. VAPOR CONCENTRATION IN GENERATION SYSTEM

Compound	Vapor concentration	
	ng/L	ppb, (v/v)
Vinyl chloride	-- ^a	-- ^a
Tetrahydrofuran	36	12
Carbon tetrachloride	14	2
Trichloroethylene	19	4
Benzene	29	9
Chlorobenzene	30	7

^aThe concentration of vinyl chloride could not be confirmed because an individual reference standard of vinyl chloride was not readily available.

Preparation of Standard Solutions

We prepared standard solutions of several volatile organic compounds in carbon disulfide. The standard solutions used during our evaluation of sorbent materials contained 88.7 µg/mL tetrahydrofuran, 159 µg/mL carbon tetrachloride, 146 µg/mL trichloroethylene, 87.4 µg/mL benzene, 86.7 µg/mL toluene, and 111 µg/mL chlorobenzene in carbon disulfide. To analyze the audit cylinder, we prepared a standard solution containing only the compounds present in that cylinder. The solution contained 294 µg/mL chloroform, 317 µg/mL carbon tetrachloride, 175 µg/mL benzene, and 325 µg/mL perchloroethylene (tetrachloroethylene) in carbon disulfide.

GC/FID Analysis

Initially, we modified the injection port of the HP-5840 GC to allow thermal desorption of 3-mm-OD sorbent tubes. This modification involved diverting the carrier gas through a sorbent tube, which was held in the injection port with an O-ring. Swagelok adapters connect the 3-mm tube to the column inside the GC oven. To analyze standard solutions, a brass tee equipped with a septum was placed in the carrier-gas line. One end of the tee was connected to an empty 3-mm tube leading to the column. Liquid injections were made through the septum and swept onto the column by the carrier gas connected to the third end of the tee. Later, we added an external heating block, mounted above the injection port, to allow thermal desorption of 8-mm-OD sorbent tubes. The heating unit consisted of an aluminum cylinder, 5.0 cm long by 4.5 cm in diameter, with a 9.5-mm hole drilled through the center of the face. A variable powerstat controlled the desorption temperature. The 8-mm-OD sorbent tube, after it was placed inside the heating unit, was connected on the top to the carrier-gas line and on the bottom to an empty 3-mm tube inside the GC injection port (see Figure 6).

We optimized the GC for the separation of six of the volatile organics: tetrahydrofuran, carbon tetrachloride, trichloroethylene, benzene, toluene, and chlorobenzene. The operating GC/FID conditions are listed in Table 4.

Calibration curves were prepared by the direct injection of standard mixtures containing known amounts of the six volatile organic compounds in carbon disulfide. From the calibration data, we calculated the equation for the linear-regression line, slope, and y-intercept.

GC/MS Analysis

GC/MS analysis was used as a confirmation for the analysis by GC/FID. Although in this work we used GC/FID to acquire preliminary data, any prepared final analytical method will require GC/MS analysis. Sorbent tubes were thermally desorbed with the GC/MS in the same manner as the GC/FID analysis. The GC/MS operating conditions are given in Table 5.

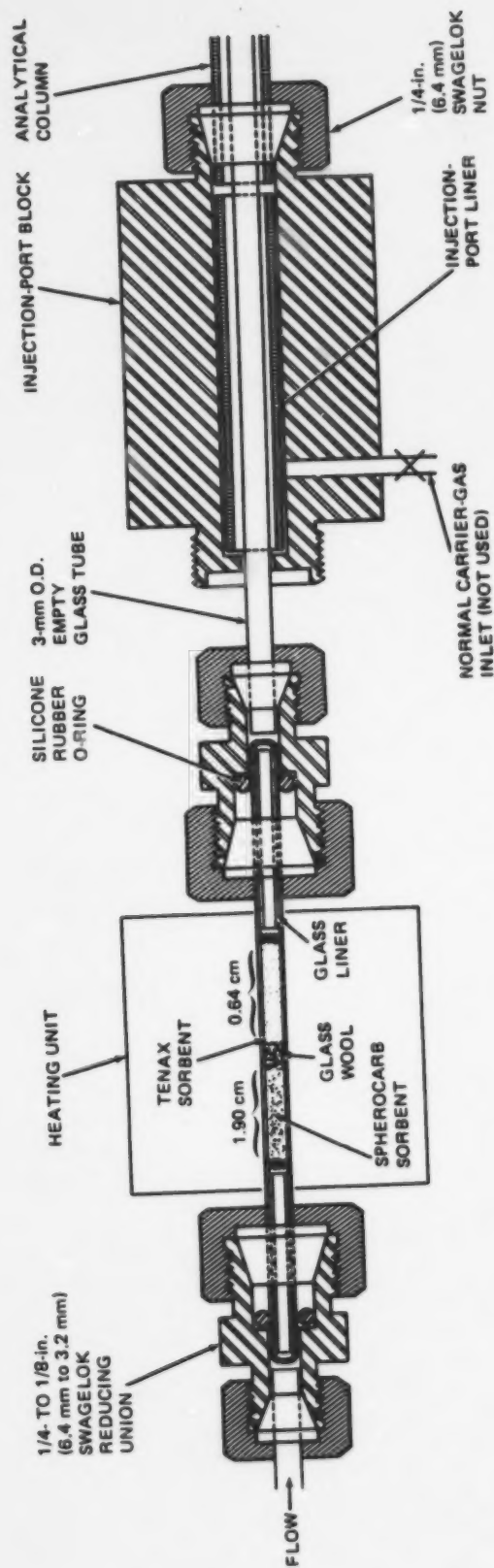


Figure 6. Diagram of thermal-desorption modification for the GC injection port.

TABLE 4. GC/FID OPERATING CONDITIONS

Instrument:	Hewlett-Packard Model 5840 gas chromatograph
Detector:	FID
Column:	1% SP-1000 on Carbopack B, 60/80 mesh, 1.8 m x 2-mm ID, glass
Temperature Program:	60 °C to 235 °C (15 min) at 15 °C/min
Injection Temperature:	200 °C
FID:	300 °C
Carrier Gas:	Helium at 17 mL/minute

TABLE 5. GC/MS OPERATING CONDITIONS

Instrument:	Hewlett-Packard Model 5985 gas chromatograph/ mass spectrometer
Column:	1% SP-1000 on Carbopack B, 60/80 mesh, 1.3 m x 2-mm ID, glass
Temperature Program:	40 °C (3 min) to 220 °C (15 min) at 8 °C/min
Carrier Gas:	Helium at 40 mL/minute
Injection Temperature:	200 °C
Mass Range:	35-260 amu
Scan Rate:	2 sec/scan

SECTION 5

RESULTS AND DISCUSSIONS

CALIBRATION

The POHCs chosen for the evaluation of the sampling system were tetrahydrofuran, carbon tetrachloride, trichloroethylene, benzene, toluene, and chlorobenzene. The retention times of selected POHCs were determined by the injection of individual compounds. The GC/FID response to each compound was determined by direct injection of a six-component standard. A representative GC/FID chromatogram of a standard mixture is shown in Figure 7. Calibration curves are shown in Figures 8 through 13, and the linear-regression data for the curves are listed in Table 6. These curves were used to estimate the linear working range for individual compounds to be used in computing recoveries during sorbent screening.

SORBENT SCREENING

Six POHCs were spiked on 3-mm tubes containing 3.8 cm of Tenax-GC. We observed 10-90% breakthrough of the six compounds with 1 min of sampling at 0.28 L/min. After 20 min (5.6 L) only three compounds were recovered: benzene--11%, toluene--35%, and chlorobenzene--69%.

The percent recovery of each compound as a function of the volume of air sampled is shown in Table 7. Although the 3-mm tube configuration is ideal for direct thermal desorption, it did not have the necessary capacity. Thus we changed to 8-mm OD tube to allow greater amounts of sorbent to be used in the sample tube.

8-mm Sorbent Tube

The recovery study was repeated with 8-mm-OD sorbent tubes spiked with the same level of volatile organic compounds. The recoveries of the compounds from Tenax, Ambersorb XE-340, Ambersorb XE-347, and Spherocarb sorbent tubes are shown in Tables 8 through 11. The data indicated that we obtained the highest recoveries for the more volatile compounds with Spherocarb and for the less volatile compounds with Tenax. Therefore, we prepared 8-mm-OD sorbent tubes packed with 1.9 cm of Tenax (front section) and 1.9 cm of Spherocarb (back section). The recovery data for this mixed sorbent tube are shown in Table 12. The data indicate good recoveries for all the compounds except carbon tetrachloride, which may be caused by a low and an erratic GC/FID response for a low concentration of carbon tetrachloride.

Capacity Tests

Initially, the generator was set up with only benzene and chlorobenzene permeation tubes, both at concentrations of about 16 ppb, to evaluate the performance of the 1.9 cm Tenax/1.9 cm Spherocarb sorbent tube. The generator was

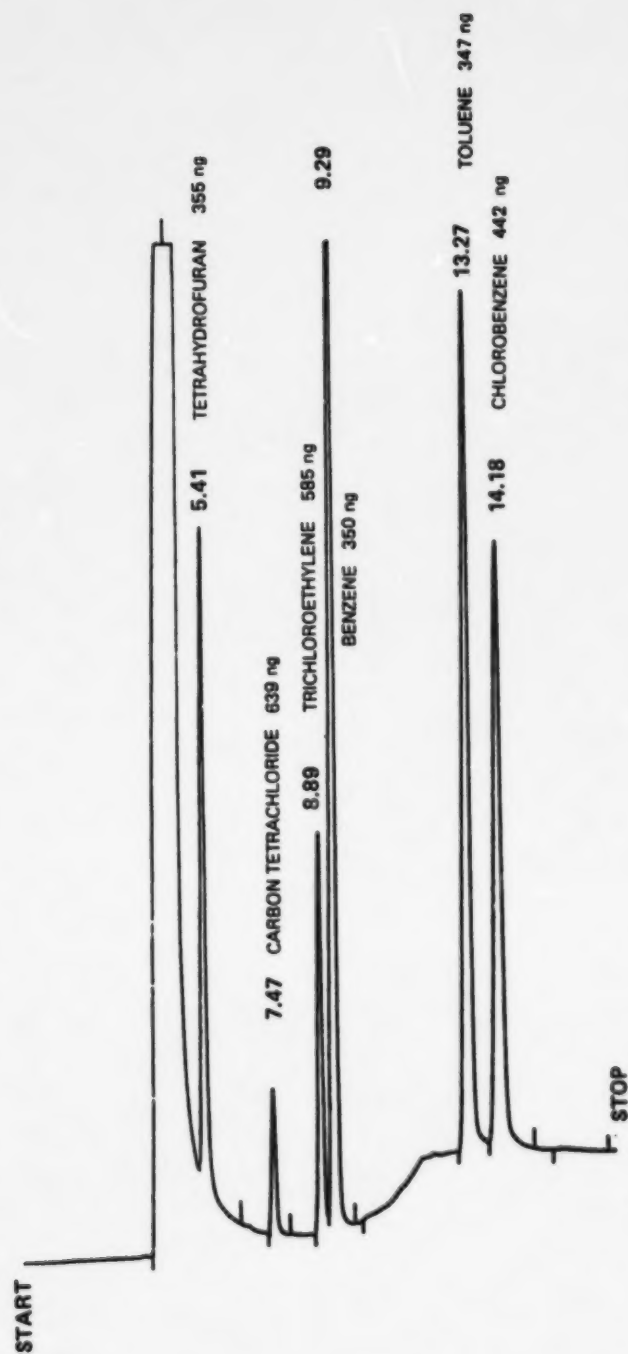


Figure 7 Chromatogram by GC/FID of a standard mixture of volatile organic compounds.

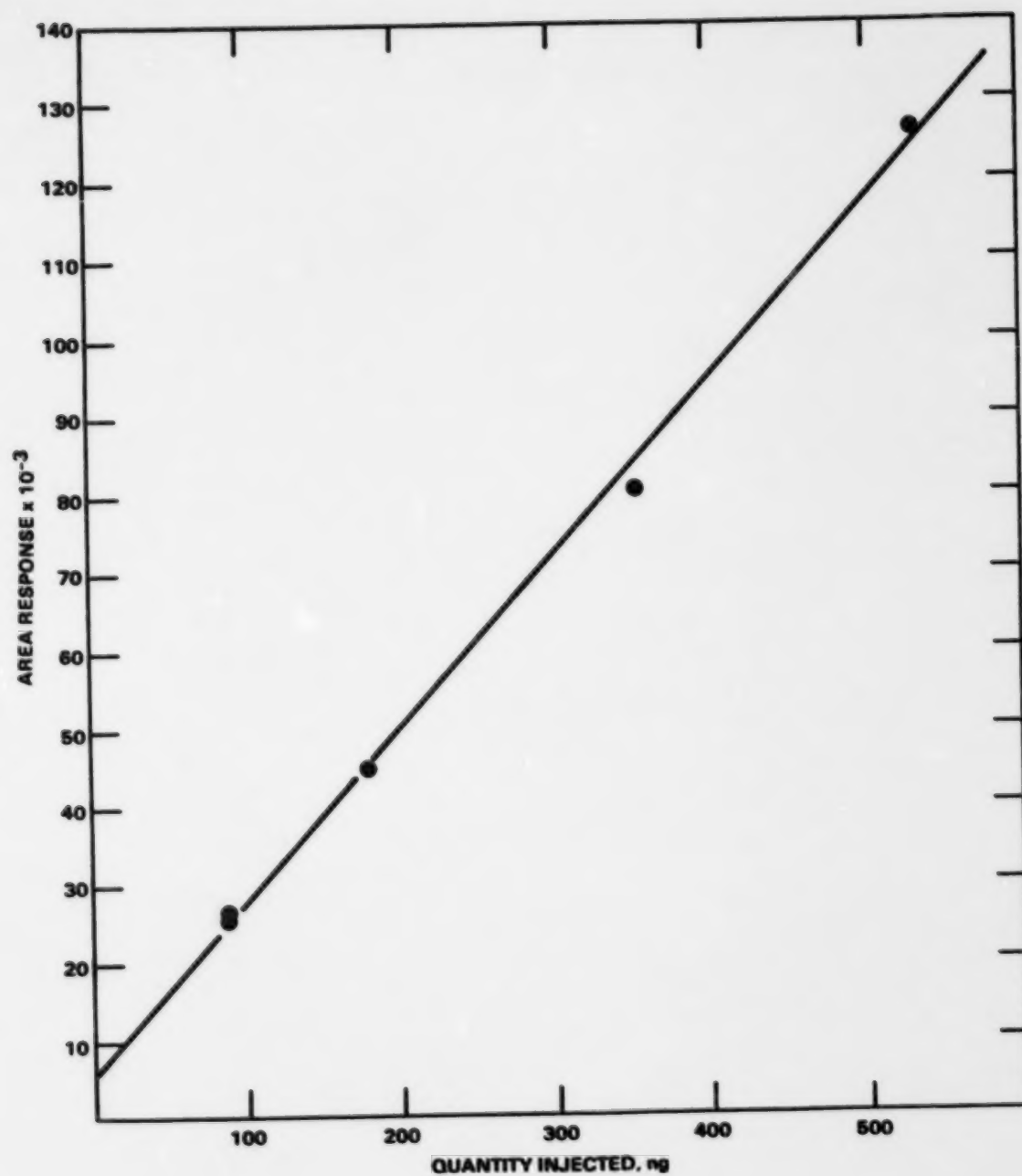


Figure 8. Tetrahydrofuran calibration curve.

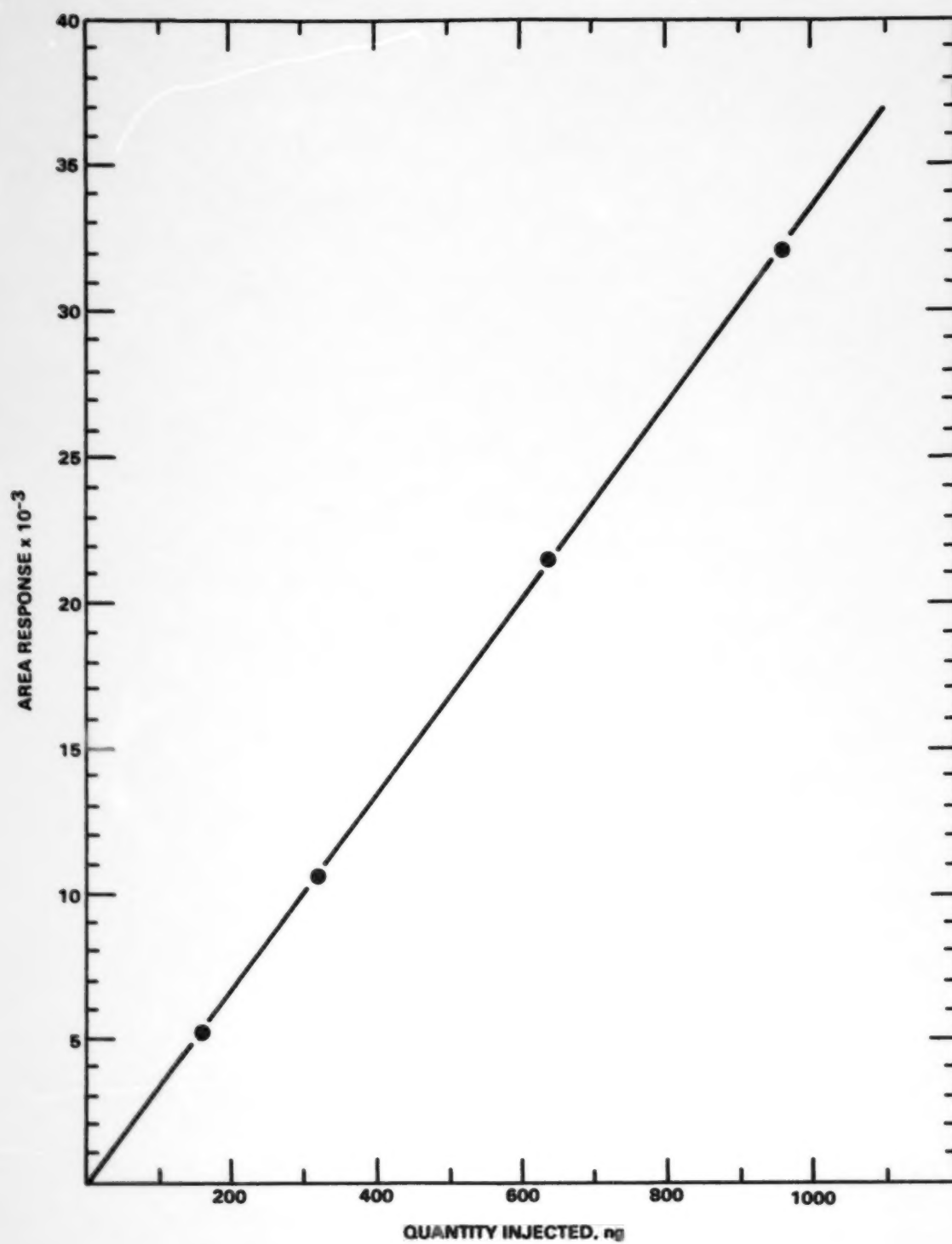


Figure 9. Carbon tetrachloride calibration curve.

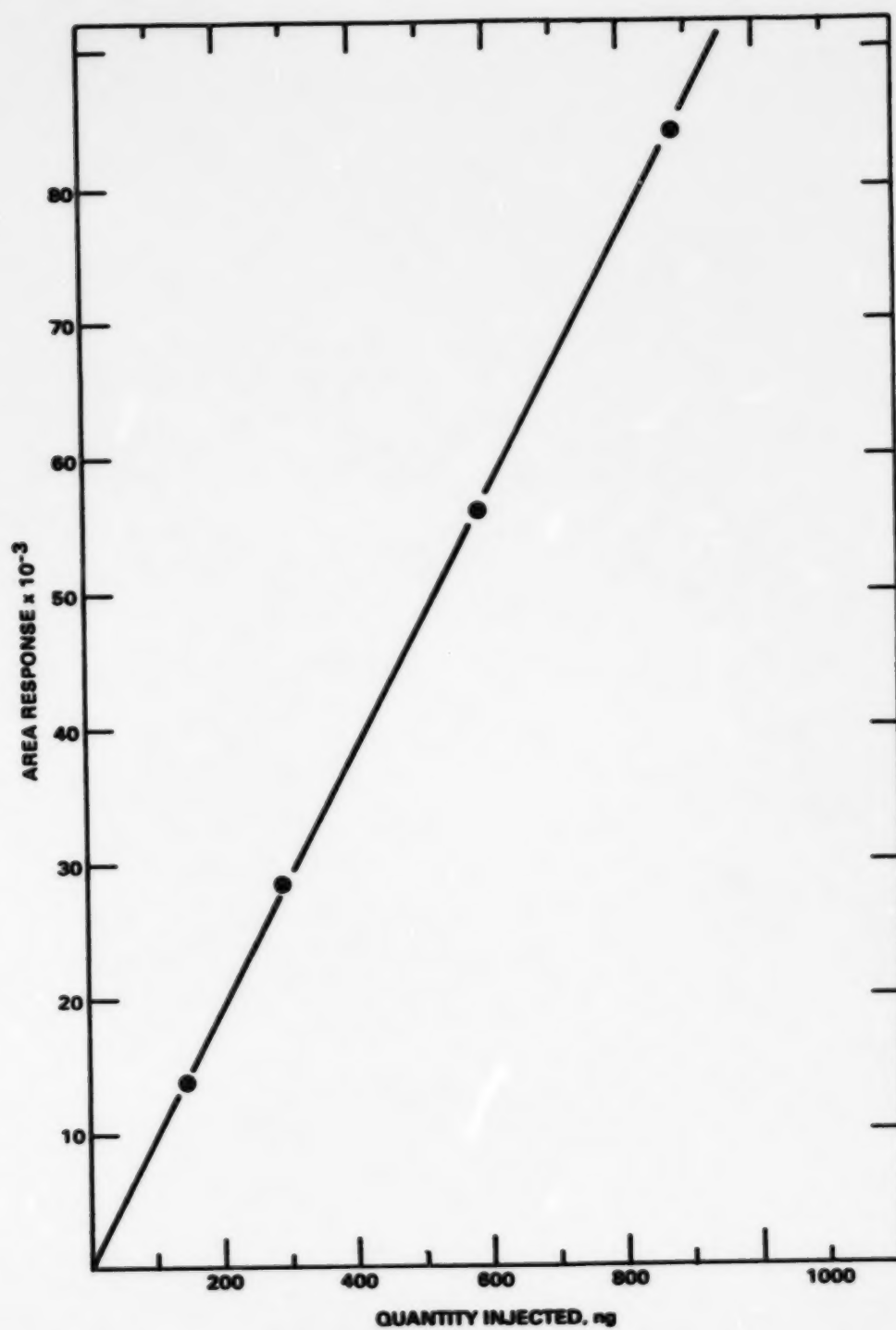


Figure 10. Trichloroethylene calibration curve.

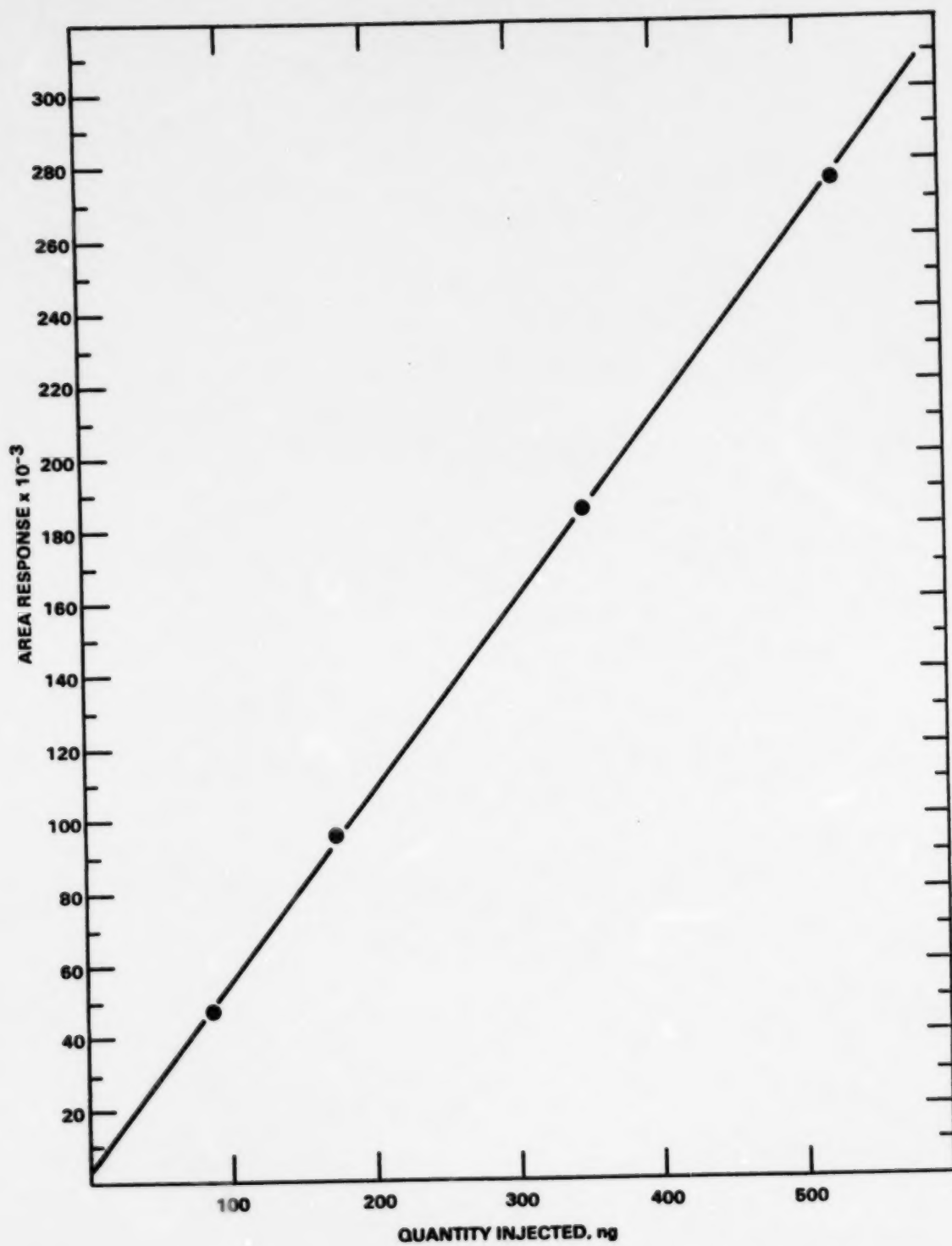


Figure 11. Benzene calibration curve.

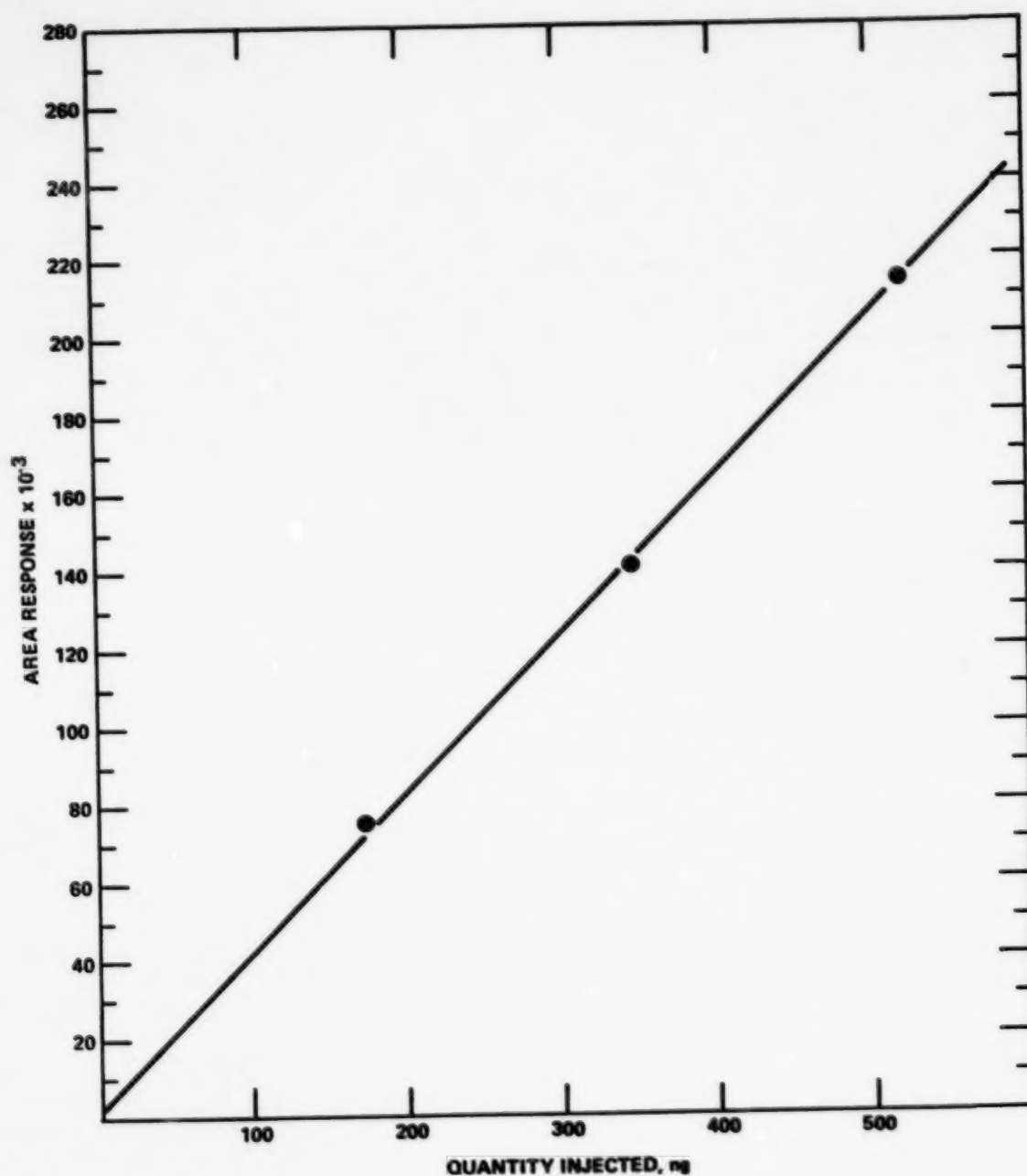


Figure 12. Toluene calibration curve.

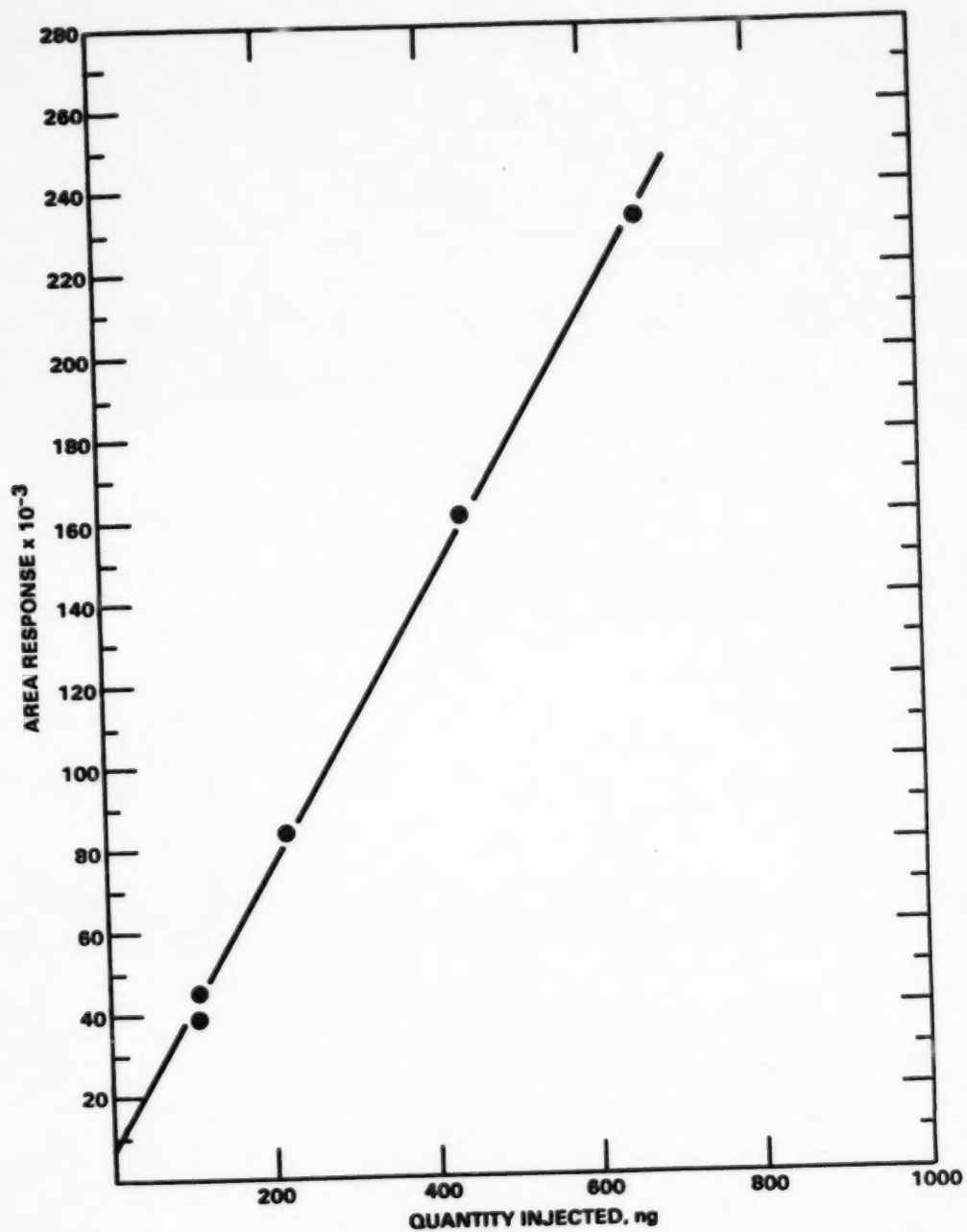


Figure 13. Chlorobenzene calibration curve.

TABLE 6. LINEAR-REGRESSION DATA FOR POHCs CALIBRATION CURVES

Compound	Range, ng	Correlation coefficient	Slope, area response/ ng	y-Intercept area response
Tetrahydrofuran	89-532	0.99843	223	5544
Carbon tetrachloride	160-958	0.99995	33.8	196
Trichloroethylene	146-877	0.99998	96.4	634
Benzene	87-524	0.99994	523	2425
Toluene	173-520	0.99960	432	2395
Chlorobenzene	110-664	0.99922	346	5316

TABLE 7. RECOVERIES OF VOLATILE ORGANIC
COMPOUNDS FROM 3-mm TENAX TUBES

Compound	Recovery, %, for volume sampled			
	0.6 L	1.4 L	2.8 L	5.6 L
Trichloroethylene	58	11	0	0
Benzene	70	-- ^a	14	11
Toluene	98	80	59	35
Chlorobenzene	103	99	91	69

^aSample interference.

TABLE 7. RECOVERIES OF VOLATILE ORGANIC
COMPOUNDS FROM 3-mm TENAX TUBES

Compound	Recovery, %, for volume sampled			
	0.6 L	1.4 L	2.8 L	5.6 L
Trichloroethylene	58	11	0	0
Benzene	70	-- ^a	14	11
Toluene	98	80	59	35
Chlorobenzene	103	99	91	69

^aSample interference.

TABLE 8. RECOVERIES OF VOLATILE ORGANIC
COMPOUNDS FROM 8-mm TENAX TUBES

Compound	Recovery, %, for volume sampled	
	0.8 L	4.0 L
Tetrahydrofuran	92	13
Carbon tetrachloride	109	39
Trichloroethylene	103	63
Benzene	103	52
Toluene	85	83
Chlorobenzene	96	93

TABLE 9. RECOVERIES OF VOLATILE ORGANIC COMPOUNDS
FROM 8-mm AMBERSORB XE-340 TUBES

Compound	Recovery, %, for volume sampled			
	1.0 L	2.3 L	4.8 L	9.5 L
Trichloroethylene	76	70	61	56
Benzene	64	24	36	40
Toluene	101	100	94	96
Chlorobenzene	90	79	61	94

TABLE 10. RECOVERIES OF VOLATILE ORGANIC COMPOUNDS
FROM 8-mm AMBERSORB XE-347 TUBES

Compound	Recovery, %, for volume sampled			
	0.9 L	2.3 L	4.5 L	9.0 L
Carbon tetrachloride	97	109	117	39
Trichloroethylene	98	89	98	83
Benzene	105	99	100	104
Toluene	113	111	113	114
Chlorobenzene	139	118	136	160

TABLE 11. RECOVERIES OF VOLATILE ORGANIC COMPOUNDS
FROM 8-mm SPHEROCARB TUBES

Compound	Recovery, %, for volume sampled			
	1.8 L	2.3 L	4.5 L	9.0 L
Tetrahydrofuran	78	94	78	60
Carbon tetrachloride	85	62	-- ^a	91
Trichloroethylene	104	149	108	91
Benzene	83	82	79	82
Toluene	91	89	87	88
Chlorobenzene	101	95	67	85

^aSample interference.

TABLE 12. RECOVERIES OF VOLATILE ORGANIC COMPOUNDS FROM
1.9-cm TENAX/1.9-cm SPHEROCARB TUBE

Compound	Recovery, %, for volume sampled	
	15 L	30 L
Carbon tetrachloride	81	-- ^a
Trichloroethylene	49	73
Benzene	84	107
Toluene	77	79
Chlorobenzene	79	85

^aSample interference.

sampled at a rate of 0.5 l/min. We sampled from 5 to 30 L on through the tube to determine capacity. However, we never reached the full capacity of the tubes. The GC/FID response, shown in Figure 14, was directly proportional to sample volume. The correlation coefficient for the benzene data was 0.9994 with a slope of 25430 area units/L and a y-intercept of 10700 area units. The correlation coefficient for the chlorobenzene data was 0.9940 with a slope of 27955 area units/L and a y-intercept of -9940 area units. These results indicate that the recovery of benzene and chlorobenzene from the mixed-sorbent tubes for all sample volumes up to 30 L was constant. Also, the data indicate that the output of the analytes from the generator was constant over the entire duration of sampling.

Evaluation of Tenax/Spherocarb Sorbent Tubes

We evaluated three different compositions of tandem-bed sorbent tubes 8-mm OD containing Tenax and Spherocarb. One sorbent tube contained 1.9 cm of Tenax (80 mg in front section) and 1.9 cm of Spherocarb (250 mg in back section). A second sorbent tube contained 1.27 cm of Tenax and 1.27 cm of Spherocarb, and a third sorbent tube contained 1.9 cm of Tenax and 0.64 cm of Spherocarb.

e The GC/FID area response for various volumes of gas mixtures of six selected POHCs sampled with the tandem-bed sorbent tubes are summarized in Tables 13, 14, and 15. Also, these tables show the slope, y-intercept, and correlation coefficient for each data set when linear regression procedures are applied to the data. The linear regression data are similar for all three types of tandem-bed sorbent tubes.

EFFECTS OF HUMIDITY

We spiked a standard solution containing six volatile organic compounds on 8-mm OD, 1.9 cm Tenax plus 1.9 cm Spherocarb sorbent tubes. We pulled clean-dry air through one set of tubes and humidified air through a second set of tubes. A third set of tubes was spiked through a Na_2SO_4 precolumn. Humidified air was then pulled through the tubes, simulating sampling through Na_2SO_4 . All tubes were thermally desorbed and the recoveries of the analytes were within a range of 96 to 139% without the Na_2SO_4 . With Na_2SO_4 , the recoveries were within a range of 88 to 110%. During the sampling of stack-gas, condensate may form as the gas cools and may pass through the sorbent tubes. To prevent this possibility, the sampling volume must be small. Also, the use of a Na_2SO_4 pretube appears to be one option to eliminate excess water from the sampling-and-analysis system without loss of analyte.

We also sampled from the vapor generator a mixture of benzene and chlorobenzene (26 ppb each) to study the effects of humidity on the sampling method using 1.9 cm Tenax/1.9 cm Spherocarb sorbent tubes with sodium sulfate pretubes. Graphs of GC area responses versus sample volumes are shown in Figures 15 and 16. Linear plots are obtained with both 50% and 75% RH conditions, indicating a constant recovery percentage, presumably close to 100%. We believe the slight difference in response at the two humidity levels was caused by a difference in the concentrations of the test-atmosphere generator. The humidified air was introduced through a separate valve, and exact duplication of the total dilution air was apparently not achieved.

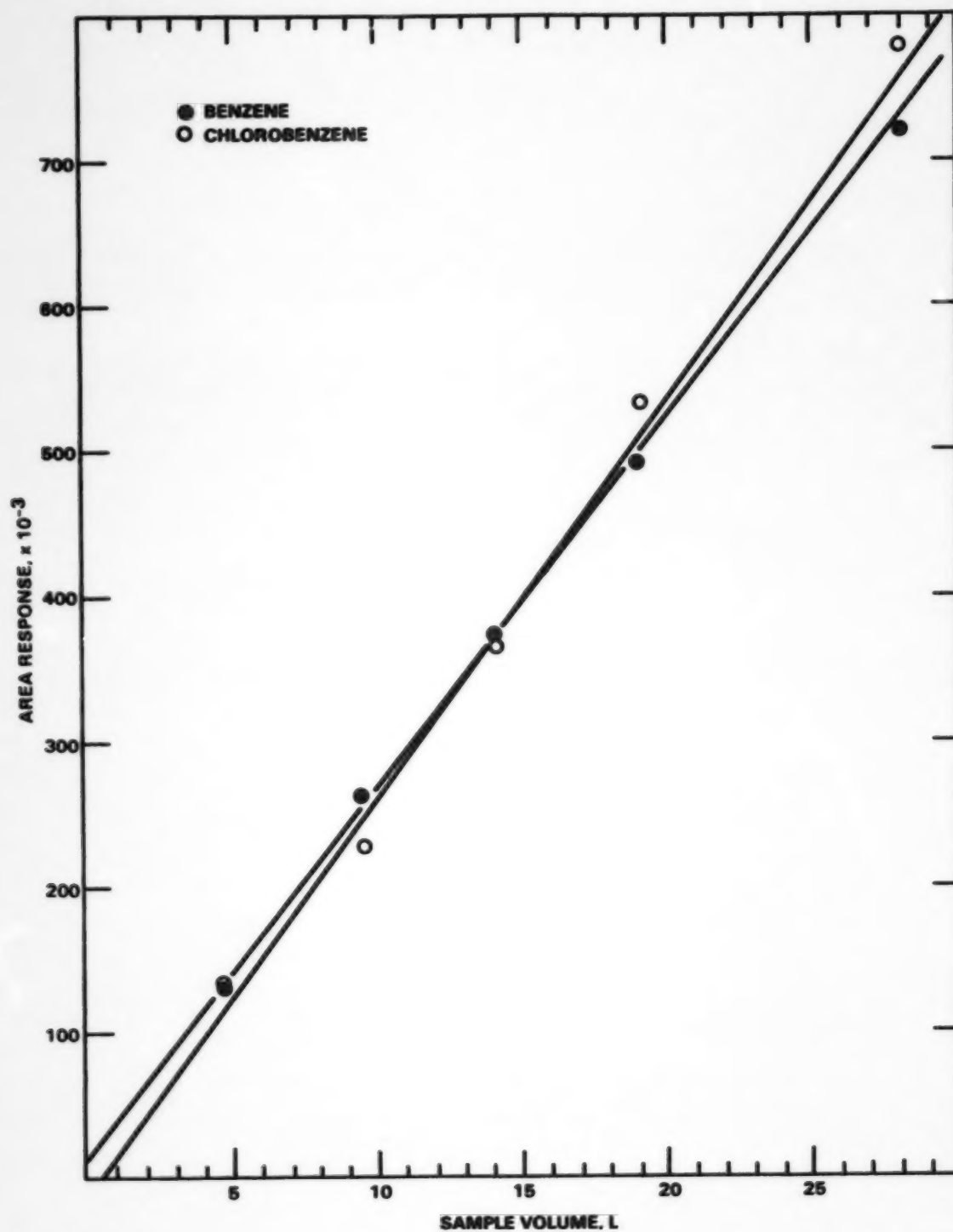


Figure 14. Comparison of GC/FID area response of benzene and chlorobenzene with total sample volume through 1.9-cm-Tenax/1.9-cm-Spherocarb sorbent tube.

TABLE 13. LINEAR REGRESSION DATA FOR GC/FID AREA
RESPONSE OF POHCs VERSUS VOLUME SAMPLED:
1.9 cm TENAX/1.9 cm SPHEROCARB

Compound	Volume sampled, L	Area response	Slope, area response/L	y-Intercept, area response	Correlation coefficient
Vinyl chloride	2.5	105100	50170	-12621	0.99937
	7.5	376500			
	15	734800			
Tetrahydrofuran	2.5	24480	7769	5678	0.99983
	7.5	64980			
	15	121800			
Carbon tetrachloride	2.5	1504	174	1572	0.83188
	7.5	3711			
	15	3843			
Trichloroethylene	2.5	4233	1425	905	0.99927
	7.5	11990			
	15	22130			
Benzene	2.5	51080	13273	22118	0.99731
	7.5	128700			
	15	218400			
Chlorobenzene	2.5	29590	10734	4968	0.99887
	7.5	89160			
	15	164500			

TABLE 14. LINEAR REGRESSION DATA FOR GC/FID AREA
RESPONSE OF POHCs VERSUS VOLUME SAMPLED:
1.27 cm TENAX/1.27 cm SPHEROCARB

Compound	Volume sampled, L	Area response	Slope, area response/L	y-Intercept, area response	Correlation coefficient
Vinyl chloride	2.5	119000	48878	-8516	0.99968
	7.5	349200			
	15	728200			
Tetrahydrofuran	2.5	22290	7603	1389	0.99835
	7.5	55260			
	15	116700			
Carbon tetrachloride	2.5	639	246	45	0.99982
	7.5	1920			
	15	3715			
Trichloroethylene	2.5	3689	1867	-1581	0.99724
	7.5	11420			
	15	26830			
Benzene	2.5	44360	11493	15241	0.99997
	7.5	100800			
	15	187900			
Chlorobenzene	2.5	24270	10709	-198	0.99877
	7.5	83960			
	15	158900			

TABLE 15. LINEAR REGRESSION DATA FOR GC/FID AREA
RESPONSE OF POHCs VERSUS VOLUME SAMPLED:
1.9 cm TENAX/0.64 cm SPHEROCARB

Compound	Volume sampled, L	Area response	Slope, area response/L	y-Intercept, area response	Correlation coefficient
Vinyl chloride	2.5	88480	50244	-32103	0.99973
	7.5	353100			
	15	718200			
Tetrahydrofuran	2.5	18150	7819	-745	0.99982
	7.5	58980			
	15	116100			
Carbon tetrachloride	2.5	824	230	146	0.99476
	7.5	1702			
	15	3668			
Trichloroethylene	2.5	3648	1339	-1330	0.96265
	7.5	5994			
	15	19840			
Benzene	2.5	39980	13604	4997	0.99986
	7.5	105400			
	15	209700			
Chlorobenzene	2.5	30890	10055	6718	0.99975
	7.5	83740			
	15	156900			

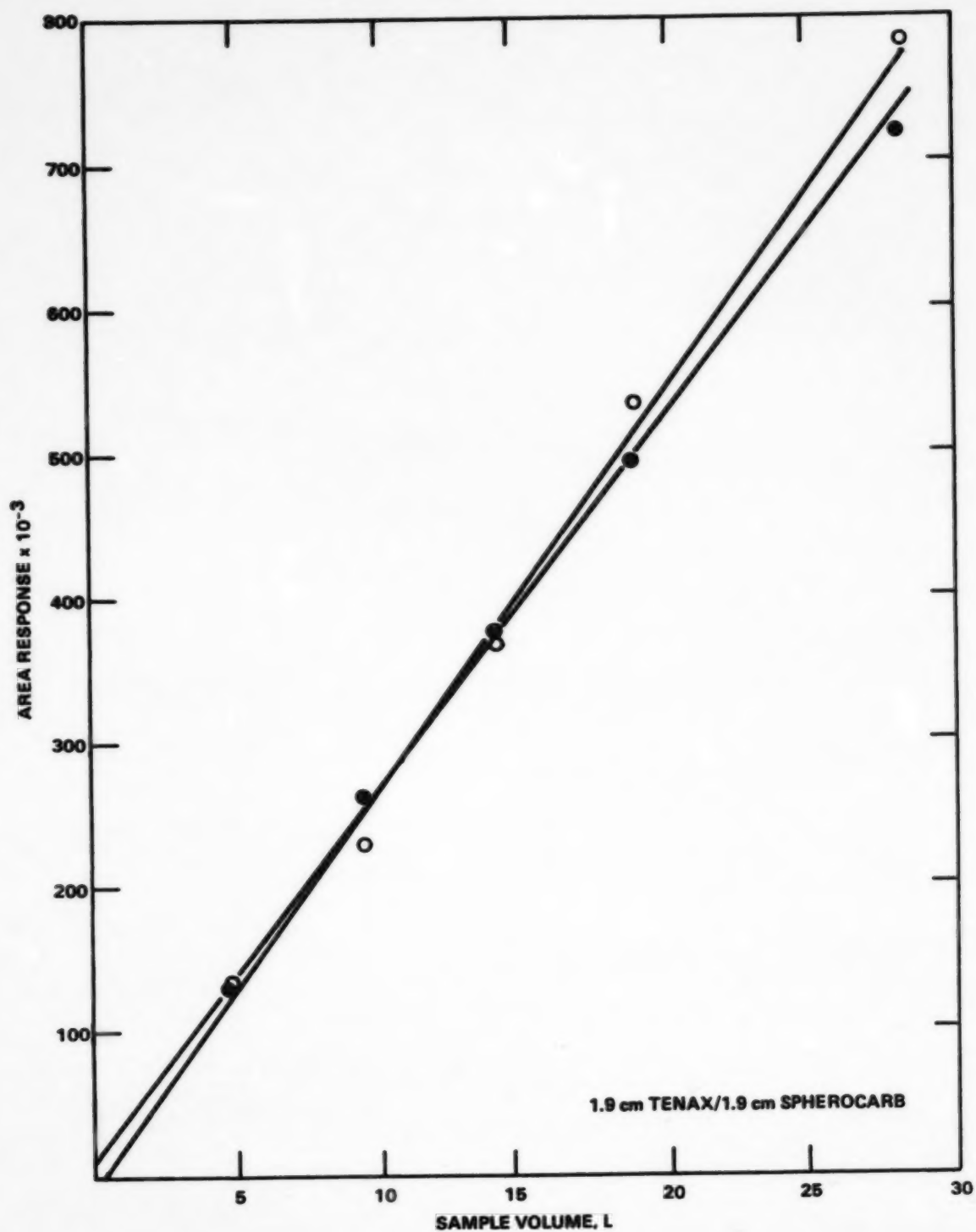


Figure 15. Comparison of area response of benzene (●) and chlorobenzene (○) with total sample volume; test atmosphere at 50% relative humidity.

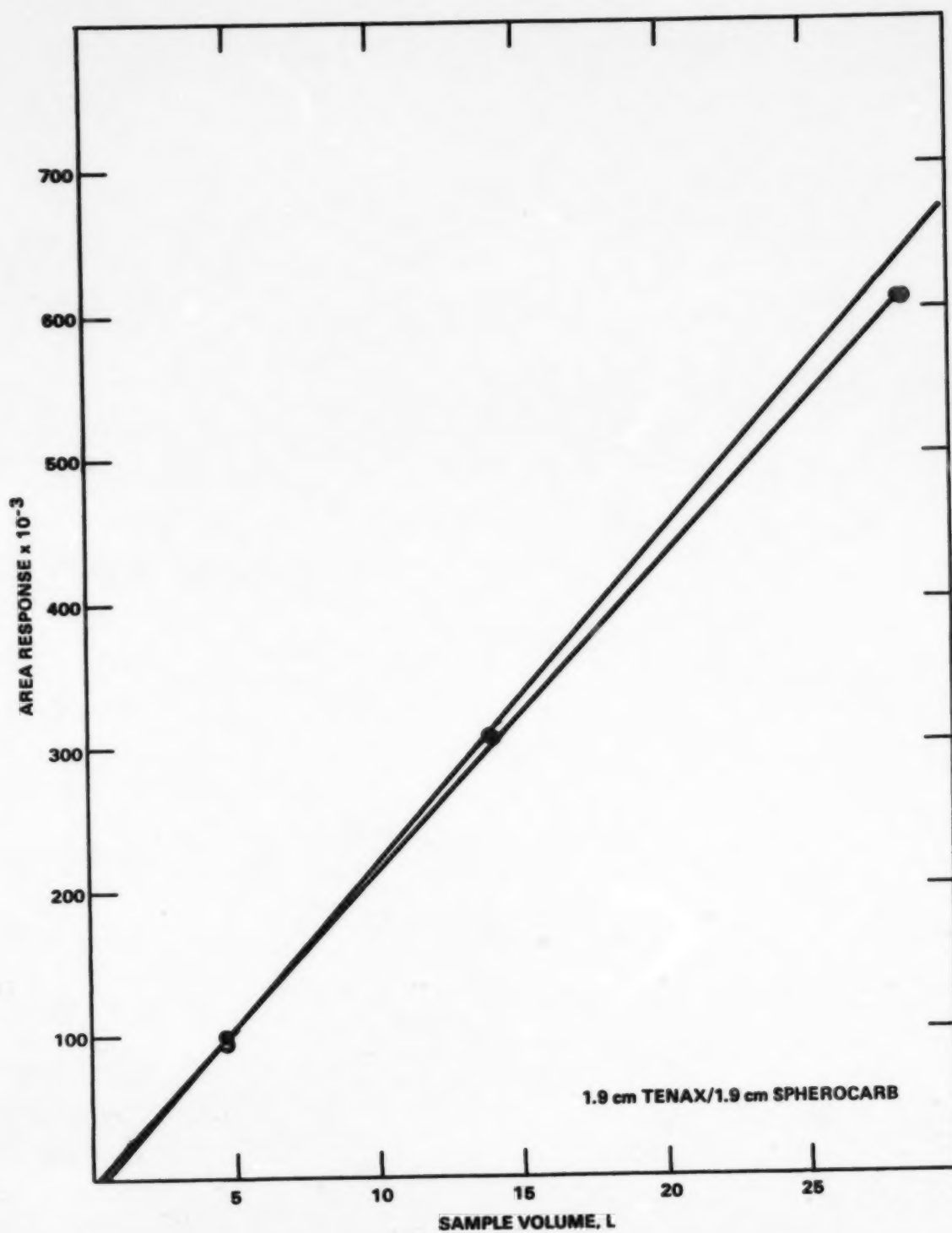


Figure 16. Comparison of area response of benzene (●) and chlorobenzene (O) with total sample volume; test atmosphere at 75% relative humidity.

STABILITY OF SORBENT TUBE SAMPLES

We tested the stability of six analytes on two Tenax/Spherocarb tube types: the 1.27-cm Tenax/1.27-cm Spherocarb tube and the 1.9-cm Tenax/0.64-cm Spherocarb tube. Duplicate tubes were used to sample 7.5 L from the generator. The tubes were capped and then stored for three days at room temperature. Recoveries for each of the analytes are listed in Table 16. Both types of Tenax/Spherocarb tubes gave greater than 85% recoveries for vinyl chloride, tetrahydrofuran, trichloroethylene, benzene, and chlorobenzene. The low carbon tetrachloride recoveries, which were less than 60% on each tube, were probably curved by low response of GC/FID. We chose the 1.9-cm Tenax/0.64-cm Spherocarb tube, shown in Figure 17, as our prototype sampling tube.

ANALYSIS OF A QUALITY ASSURANCE AUDIT CYLINDER

We analyzed the contents of an audit cylinder, Volatile POHC Quality Assurance Cylinder #1849 (provided by EPA), using a 1.9-cm Tenax/0.64-cm Spherocarb sorbent tube. The cylinder contained low concentrations of five volatile organic compounds in nitrogen: vinyl chloride, chloroform, carbon tetrachloride, benzene, and perchloroethylene. In Table 17 we have listed the area response of each compound in the audit cylinder as a function of volume sampled. We used the calibration curves obtained from spiked sorbent tubes to calculate the concentrations of organic compounds in the audit cylinder. The concentration values found and the EPA reference values are listed in Table 18.

The concentration found using the tandem-bed sorbent tube agree with the EPA reference concentrations except for carbon tetrachloride. As in earlier experiments this value is significantly lower than the reference values.

GC/MS Analysis

A GC/MS experiment was performed using standards spiked on sorbent tubes from carbon disulfide solution. The large solvent tail from the standard prepared in carbon disulfide made comparison with the gas samples from the audit cylinders difficult.

These data indicate that calibration standards should be prepared by sampling gas standards onto the sample tubes. The data presented in Table 17 also point to the use of this technique because we obtained linear relationships between the sample volume and the FID response for all five compounds in the audit cylinder. The GC/MS experiment was not repeated using gas standards because of a lack of time to perform the experiment before the end of the contract.

TABLE 16. RESULTS OF THE STABILITY STUDY

Compound	1.27 cm Tenax/ 1.27 cm Sphero carb, % recovery	1.9 cm Tenax/ 0.64 cm Sphero carb, % recovery
Vinyl chloride	112	118
Tetrahydrofuran	90	85
Carbon tetrachloride	43	62
Trichloroethylene	89	100
Benzene	87	98
Chlorobenzene	110	108

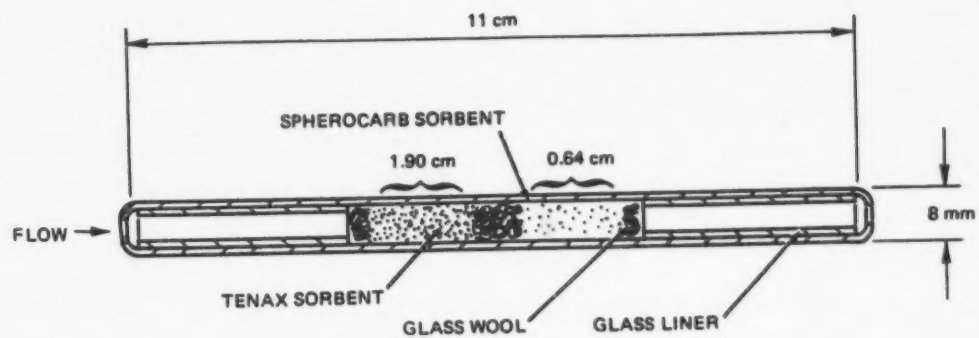


Figure 17. Drawing of prototype sample tube.

TABLE 17. GC/FID AREA RESPONSE OF VOLATILE ORGANIC
COMPOUNDS IN AN AUDIT CYLINDER NO. 1849^a

Compound	Volume sampled, L, at 0.5 L/min			
	2.5	2.5	5.0	10
Vinyl chloride	171800	173800	350800	700800
Chloroform	52100	52910	99220	195600
Carbon tetrachloride	34570	33540	66380	135400
Benzene	386700	373700	582600	1219000
Tetrachloroethylene	162600	160200	304900	571100

^aResults in arbitrary peak area limits.

TABLE 18. COMPARISON OF AUDIT CYLINDER RESULTS

Compound	Concentration found, ppb	EPA reference concn, ppb
Chloroform	110	123
Carbon tetrachloride	70	127
Benzene	120	140
Trichloroethylene	125	129

SECTION 6

QUALITY-ASSURANCE SUMMARY

The work that was done at SoRI and presented in this report was performed under SoRI Quality Assurance plan for Contract 68-02-3696, Work Assignment 014, Amendment 0, January 14, 1985. Although the project includes environmentally related measurement activities, SoRI was not involved in field sampling or the preparation of field samples for analysis. Thus, sampling procedures, chain-of-custody procedures, and spiked-sample matrixes were considered not applicable to the systematic review of this project. The major efforts of SoRI were to evaluate sorbent materials, to develop a rugged sampling tube, and to evaluate the sampling system in the laboratory with six volatile organic compounds.

An internal audit of the project revealed no deficiencies in the internal quality-control checks and data processing. Those items that were reviewed include research notebooks, instrument logs, printouts for GC/FID and GC/MS chromatograms, and standard preparations. Because this work was primarily associated with feasibility techniques and not repetitive measurements, data-quality indicators were not available.

Our task was to demonstrate the feasibility of a simplified design for a sampling system for medium levels of volatile organic compounds. Our goal was to meet or surpass the recovery reported for the VOST (4). For the VOST, the range of averaged recovery for a single pair of sorbent tubes were 43-142% for vinyl chloride, 40-108% for carbon tetrachloride, 79-132% for trichloroethylene, and 90-153% for chlorobenzene. With our system we obtained recoveries of 89.4% for chloroform, 55.1% for carbon tetrachloride, 85.7% for benzene, and 96.8% for trichloroethylene. These data were determined from the analysis of an EPA audit cylinder.

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